pH and Titratable Acidity

Determination of [H^+] and various acid compounds in musts and wines

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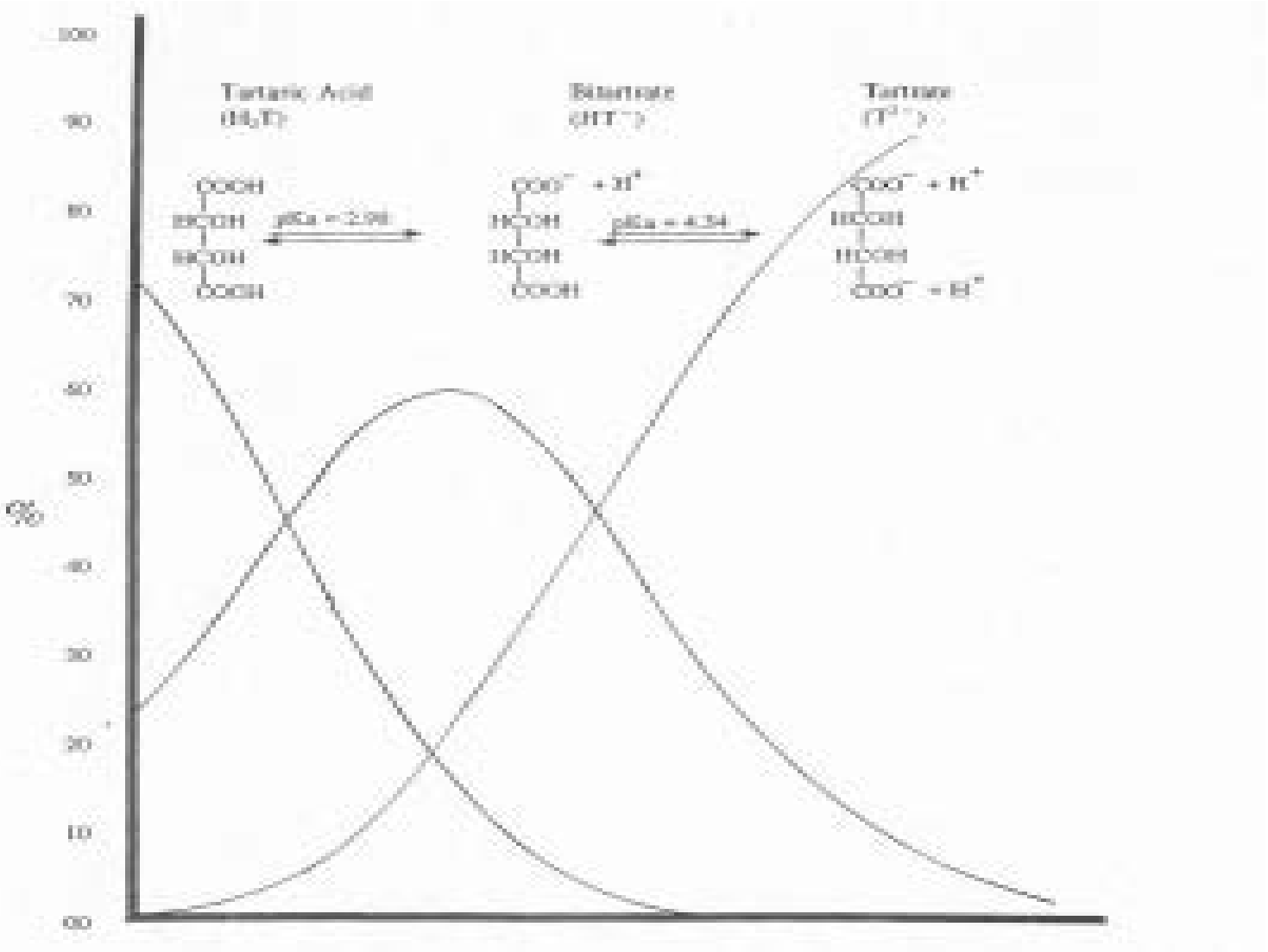
What are Acids

- Acids dissociate to produce protons (hydrogen ions) in solution
- Acids found in juices and wines are termed “weak acids” – they only partially dissociate
- Tartaric, malic, and small amounts of citric found in grapes
- Tartaric, malic/lactic, succinic acids are primary in wines



2.5 3.0 3.5 4.0 4.5 5.0 5.5

What are Acids

- During alcoholic fermentation sugars are converted into succinic acid
- During the malo-lactic fermentation malic acid is decarboxlated to form lactic acid
- Some acetic acid can be formed during both fermentation in small amounts
- Wines exposed to excessive oxygen can have growths of acetobacter which produce acetic acid and ethyl acetate (spoilage markers)

Bases

- Bases are chemicals that can accept protons
- In water strong bases produce a hydroxyl ion, OH^-, which can react with acid protons
- Bases are used as analytical reagents in titrations of strong and weak acids

pH

- pH is a concentration term for free (dissociated) protons in solution
- pH = – log[H^+], the logarithmic concentration of free protons with the sign changed (to make pH values positive numbers)
- On the pH scale values below pH 7 denote acidic solutions, values above 7 denote alkaline or basic solutions

pH

- Consult operator's manual for standardization using two buffer solutions.
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- Rinse the beaker with sample. Place enough fresh sample in beaker to cover electrode junctions. Allow to come to defined temperature.
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- Place electrode(s) in the sample.
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- Allow meter reading to stabilize and record value.

pH

- Buffers (pH 7.00 and 4.00): Prepared buffers with indicators for detection of dilution or breakdown are commercially available through chemical supply houses.
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- Buffer (pH 3.55): Add approximately 5 g potassium acid tartrate to 500 mL deionized water. Mix on magnetic stirring table for 5 min. Allow undissolved crystals to settle and decant, filtering as necessary. At 25^0 C, the pH of this solution is 3.55.

pH

- Do not remove electrodes from buffer or sample solutions while instrument is responding. During changing of samples, the meter should be in the "stand-by" mode.
- When not in use and between measurements, store electrodes according to manufacturer's recommendations.
- The reference side of the combination electrode should be checked routinely to ensure an ample supply of KCl filling solution. The level should not be allowed to drop much below the filling port. This port must be uncovered during use.

Titratable Acidity

- Titratable Acidity (TA) refers to the total concentration of free protons and undissociated acids in a solution that can react with a strong base and be neutralized
- Typical concentrations of free protons in a juice or wine range from ~ 0.1 to 1 mg/L, whereas TA values might be 4 to 8 g/L

Titratable Acidity

- A Titratable Acidity (TA) titration will generally use the strong base, NaOH, and either a chemical indicator or pH meter to signal when equivalent amounts of base have been metered into the sample
- The concentration of sodium hydroxide used is typically 0.1 N or less

Normality vs. Molarity

- Two units used to express the concentration of an analytical reagent
- Molarity denotes the concentration in moles of reagent per liter, eg. Mol NaOH/L
- Normality denotes the concentration in moles of reacting unit per liter, eg. Mol OH^-/L
- For solutions of NaOH the Normality equals the Molarity

TA MEASUREMENTS

- NaOH (0.100 N or 0.100 M) in buret
- Standard 0.100 M HCl or KHP (200 mg) in beaker
- Add phenolphthalein indicator (1 drop) or insert pH electrodes
- Add base from buret to endpoint
- $N_{NaOH} = V_{HCl} \times M_{HCl} / V_{NaOH}$
- TA (g/L H_2T) = $V_{NaOH} \times N_{NaOH} \times (0.150/2) \times 1000/5$

TA ANALYSIS + FORMOL NITROGEN ANALYSIS

- Two burets with NaOH (0.100 N and 0.0100 N)
- **Pre-titration**
- Pour a few mL juice or wine sample into small beaker
- Insert pH electrodes and enough DI water to cover electrode
- Add base from buret to pH 8.2 endpoint (V_1)
- **Titration**
- Accurately pipette a 5mL juice or wine sample into the beaker and note volume reading on buret
- Add 0.1 N NaOH from buret to pH 8.2 endpoint and note volume reading (V_2). V_{NaOH} = finalV_2 – V1

TA ANALYSIS + FORMOL NITROGEN ANALYSIS

- **Titration**
- Accurately pipette a 5mL juice or wine sample into the beaker and note volume reading on buret
- Add 0.1 N NaOH from buret to pH 8.2 endpoint and note volume reading (V_2).
- $V_{NaOH} = V_2 - V_1$

TA RESULTS

- $V_{NaOH} = V_2 - V_1$ using 0.1 N NaOH
- TA (g/L H_2T) = V_{NaOH} x N_{NaOH}x(0.150/2) x 1000/5
- TA (g/L H_2T) = V_{NaOH} x 1.5

TA ANALYSIS + FORMOL NITROGEN ANALYSIS

- **Nitrogen**
- Pre-titrate formaldehyde to pH 8.2
- Add 2 mL formaldehyde to juice/wine sample and titrate with 0.01 N NaOH from buret to pH 8.2 endpoint
- Note beginning volume reading and endpoint volume reading (V_3 and V_4)

- $V_{NaOH} = V_4 - V_3$

- $N\ (mg/L) = V_{NaOH} \times N_{NaOH} \times 14 \times 1000/5$
- $N\ (mg/L) = V_{NaOH} \times 28$ using 0.01 N NaOH

TA ANALYSIS + FORMOL NITROGEN ANALYSIS

- **Nitrogen**
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